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FINAL TECHNICAL REPORT

BY

BURKE RESEARCH COMPANY
POMPANO BEACH, FLORIDA

TO

UNITED STATES ARMY ORDNANCE
TANK-AUTOMOTIVE COMMAND
CENTERLINE, MICHIGAN

COGNIZANT ORDNANCE DISTRICT OFFICE
U. S. ARMY ORDNANCE DISTRICT
BIRMINGHAM, ALABAMA

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SURFACE APPLICATION OF ANTIOZONANTS
TO RUBBER ITEMS AND EVALUATION OF
ANTIOZONANTS FOR PACKAGING RUBBER
ITEMS IN PLASTIC BAGS

CONTRACT NO. DA-20-018-ORD-22837

PERIOD COVERED: JUNE 1, 1960 to NOVEMBER 17, 1961

REPORT BY:

DR. E. E. STAHLY
B. P. HUNT

DECEMBER 1, 1961

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COMPANY PURSUANT TO CONTRACT
NO. DA-20-018-ORD-22837.
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ABBREVIATIONS USED IN THIS REPORT

GR-S	Butadiene-Styrene synthetic rubber
SBR	Synthetic rubber (present designation for GR-S rubbers)
pd	phenylenediamine
p-pd	p-phenylenediamine
DETA	diethylenetriamine
TETA	triethylenetetramine
TEPA	tetraethylenepentamine

I. Objective

The objective of the contract was written as follows:

"Develop methods of surface applications of antiozonants to rubber items and evaluate antiozonants for packaging rubber items in plastic bags."

In preliminary discussions, Detroit Arsenal R & D personnel suggested that Burke Research Co. concentrate their early efforts on the phase of "packaging rubber items in plastic bags". Thus "methods of surface application of antiozonants to rubber items" received later and lesser attention in this contract.

II. Introduction

This report summarizes the work done by the Burke Research Company from June 1, 1960 to November 17, 1961, under contract DA-20-018-ORD 22837, a prime objective of which was item 6 of the Requirements: "Evaluate antiozonants (in accelerated tests) for packaging of rubber items in plastic bags which will retain vapors of the antiozonants in part or in total during storage for long periods of time." Data for item 7 stemming from item 6 are also supplied. Item 7 reads "-----conduct ozone tests of rubber samples placed in plastic bags together with various volatile antiozonants -----".

Personnel of the Detroit Arsenal had expressed their belief that polyethylene bags alone would afford considerable protection against ozone attack to rubber items stored in them, and that volatile antiozonants in pill form could be included in this type of packaging as a convenient means of providing additional protection. For example, tires on stored vehicles could be enclosed in polyethylene bags, but could not be hermetically sealed therein and an antiozonant might afford protection against ozone which would enter by diffusion particularly through the bag closure.

The Burke Research Company has evaluated antiozonants primarily in terms of their suitability for this particular bag application. In accordance with the broader objectives of the contract, some supplementary investigations were conducted, particularly relating to the methods of applying packaging antiozonants, e.g., by vapor coating and dip-coating. Spray-coating of rubber items, a part of points 1 to 5 of the Requirements of the contract, was initially postponed at the request of Arsenal R & D personnel, to permit study of other methods of application such as vapor-coating by exposure of rubber samples to vapors, and dip-coatings from solutions which were considered more practical methods of use. The aerosol-spray application

required no constructive development work, since "spray-can" manufacturers will "can" any materials specified by a consumer. The time of the contract did not permit actual "canning" of antiozonants, spraying rubber items therewith, and testing of the sprayed items.

Thus this report covers (1) tests of packaging rubber items in polyethylene bags together with various antiozonants, and (2) tests of surface-coated samples wherein the coatings were applied either by exposure to vapors, or by dip-coating from solutions. The vapor exposure method is believed to carry a minimum of toxicity and fire hazard, no drying time, and good protection against ozone attack, approaching that obtained with the more hazardous solution dipping method.

III. Brief Statement of Results

One hundred and eleven commercial chemicals were evaluated as antiozonant materials for packaging rubber items. Both accelerated screening (short range) and storage (long range) tests were conducted at about 100 \pm 5 pphm ozone (at 40°C.).

Complete protection of SBR-1500 loops in vented bag tests was afforded for 54 weeks in an atmosphere of ozone @ 100 \pm 5 pphm at 40°C., by use of the following packaging additives:

Tetraethylenepentamine
Dicyclohexylammonium nitrite
o-Phenylenediamine
m-Phenylenediamine
p-Phenylenediamine
Triethylenetetramine (by interpolation of results)

These tests are continuing.

In addition to the above additives, in vented jar or vented bag tests under the same test conditions complete protection was afforded SBR-1500 loops by the following additives in tests still continuing:

<u>Additive</u>	<u>Weeks (to date)</u>
Menthanediamine	44
Polyamine H Special	44
Tetrabutylthiourea	44
Furfurylamine	44
Diethylenetriamine	27
Dodecylamine (90%)	25
2,5-Dimethylpiperazine	27
Diisopropylammonium nitrite	27
Triethylenetetramine	27 (by interpolation)

In addition to the above additives, the following materials showed complete protection to SBR loops in "closed bag" tests still continuing.

<u>Additive</u>	<u>Weeks</u>
N,N'-Dimethyl-N,N'-di-(1-methyl-propyl)-p-phenylenediamine	54
Ditto with 1.5 parts wax	59
N,N'-Di-3-(5-methylheptyl)-p-phenylenediamine	54
2,6-Diaminopyridine	54
2,7-Dimethylquinoline	54
Anthracene	54
Hydroquinone	54

<u>Additive</u>	<u>Weeks</u>
N-Phenyl-N'-isopropyl-p-phenylenediamine	54
Phosphorous pentasulfide	54
6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	54

Dip-coating tests showed no cracking of SBR loops in over 7 months exposure to 100±5 pphm ozone at 40°C for the following:

N-n-Butyl-p-aminophenol
N,N'-Di-sec-butyl-p-phenylenediamine
N,N'-Di-2-octyl-p-phenylenediamine
N,N'-Di-3-(5-methylheptyl)-p-phenylenediamine.

It was also found that residual protection is afforded SBR-1500 by pre-exposure of samples to various additives, such pre-exposure giving protection to 100 pphm ozone for two to three months, and to <10 pphm ozone for more than 4 months in tests which are being terminated by the ending of the present contract. The additives which appear to be of continuing interest for further study in these pre-exposure and residual protection tests are:

Diethylenetriamine
Menthanediamine
Furfurylamine
Polyamine H Special
Triethylenetetramine
Tetraethylenepentamine
6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline.
Phosphorus pentasulfide

The photographs in Appendix E demonstrate the effective use of packaging antiozonants.

A continuation of this work on an extension of the present contract would allow further study of the above materials as well as study of analogous compounds and their derivatives modified to adjust volatility and/or reactivity characteristics. Since tests were terminated early by the ending of the contract, selection of additives which give longest protection cannot be made. Testing must run to the point of failure before most active additives are known.

One other facet of these tests is to be studied in continuation of the present contract, namely the over-cure resulting with additives such as tetrabutylthiourea, salts of alkyldithiocarbonic acid, and phosphorus pentasulfide. While giving packaging protection, these sulfur-containing additives tend to over-cure the surface of the rubber items, and before final recommendations or selections can be made of effective additives, the tensile properties of the rubber sample should be examined after storage for periods of increasing duration.

IV. Detailed Summary

A) Testing Methods

1. Long and Intermediate Term Packaging Tests

Of the various test methods used in the evaluation of packaging antiozonants, those most closely approximating conditions of practical use were the "bag tests" in which two loops of SBR (compounded without wax or other protective materials) were enclosed with one gram of pilled antiozonant in a 4-mil polyethylene bag, either "closed" or slightly "vented", and the bag was then hung in an ozone cabinet maintained at an ozone concentration of 100 ± 5 pphm and temperature of 40°C . A variation of the vented bag test employed pint glass jars with similar venting. The designated "closed" bag test was not hermetically sealed, but allowed a minimum of diffusion through the closure.

2. Screening Tests

Because of the inherent slowness with which the packaging tests yielded results, "screening" tests were set up in which the SBR specimens were exposed to greater concentrations of ozone by means of greater ventilation of the "package". In the screening tests the package consisted of a pint jar covered with polyethylene in which were punched six 5.5 mm holes. The resultant amount of ventilation also allowed a relatively rapid escape of antiozonant vapors, and to compensate for this, an excess (5g) of antiozonant was used.

3. "Vapor Pre-Coating" Test

The residual protection imparted to SBR loops by exposure to antiozonant vapors was tested by the enclosure of the loops together with antiozonants for various periods of time before direct exposure of the loops to ozone at either (a) 100 pphm or (b) less than 10 pphm concentrations.

4. Effect of Antiozonant Vapors on Tensile Properties of SBR

To determine the effects of antiozonant vapors on the tensile properties of SBR-1500, dumbbells were enclosed with antiozonants at room temperature for thirty days, at the end of which period, tensile values were obtained on the dumbbells.

5. Alternate Methods of Applying Packaging Antiozonants

Some of the antiozonants evaluated by one or more of the above tests were also subjected to tests involving a different method of application of the antiozonant (i.e., a method different from that of "vapor-precoating" in the package). In "dip-coating" tests, loops were dipped into antiozonant solutions, allowed to drip-dry and then were directly exposed to 100 pphm ozone. In "antiozonant-impregnated wrapping" tests, SBR loops draped with a single layer of cheesecloth impregnated with one gram antiozonant were placed in pint jars which were vented and exposed to ozone as in the screening test.

B) Significant Test Results and Conclusions

- 1) Quite a number of the materials tested as packaging antiozonants substantially increased the period of protection beyond that given by the packaging alone (Appendix D-2). Those which afforded complete protection to SBR loops packaged with them in vented bags or jars for the duration of their test periods are listed below. These tests should be continued to determine the maximum duration of protection.
 - a. Tetraethylene pentamine, dicyclohexylammonium nitrite, o-phenylenediamine, m-phenylenediamine, and p-phenylenediamine (tested for 54 weeks in vented bags).
 - b. Menthanediamine, Polyamine H Special, (1) tetrabutylthiourea, and furfurylamine (tested for 44 weeks in vented jars; tests terminated by ending of contract and not by failure).
 - c. Diethylenetriamine, dodecylamine, (2) 2,5-dimethyl piperazine, and diisopropylammonium nitrite (tested for 25 - 27 weeks in vented bags). Tests should be continued.
 - d. Triethylenetetramine was not tested in a vented bag or jar, but results of other tests to which it was subjected indicate that it is at least as effective a packaging antiozonant as tetraethylenepentamine.
- 2) When the above-tested materials were tested further to determine the residual protection imparted by them, and the effects of their vapors on tensile properties of SBR, the following conclusions were made (Appendix D-7):

(1) Union Carbide Chemical Co.

(2) Armeen 12D, Armour Chemical Co. (90% C₂amine)

- a. Diethylenetriamine is the most effective of all the materials tested, particularly in regards to the speed with which it produces a highly protective residual effect. It has a slight tendency to produce overcure, the rubber sample losing about 10% of its tensile strength in 30 days.
 - b. Menthane diamine, Polyamine H Special, triethylenetetramine, tetraethylenepentamine, furfurylamine and dodecylamine seem to be the best of the materials tested from the standpoint of imparting a high degree of residual protection without producing a serious degree of overcure. Dodecylamine is less effective than the other four compounds, but its slight softening effect might prove to be an advantage in long term storage of rubber. Furfurylamine because of overcure on longer storage of samples may prove unusable, and requires further study.
 - c. Diethyldithiocarbamic acid as the diethylammonium salt, tetrabutylthiourea, and piperidinium pentamethylene dithiocarbamate (the latter was not included in packaging tests) were very effective in preventing ozone cracking, but these sulfur-containing additives caused a pronounced surface overcure of SBR exposed to their vapors, and therefore may be less advantageous where high tensile properties are to be maintained in the packaged item.
 - d. 2,5-Dimethylpiperazine, the o-,m-, and p-phenylenediamines, dicyclohexylammonium nitrite (and presumably diisopropylammonium nitrite, although it was not included in the "vapor pre-coating" tests) imparted considerably less residual protection than did the other materials listed above in sections a, b, and c.
- 3) Packaging antiozonants which, although failing in vented bag tests, have given complete protection in closed bag tests (for at least 54 weeks) are N,N'-dimethyl-N,N'-di-(1-methylpropyl)-p-pd (1), N,N'-di-3-(5-methyl-heptyl) -p-pd (2), 2,6-diaminopyridine, 2,7-dimethylquinoline, anthracene, hydroquinone, N-phenyl-N'-isopropyl-p-pd, phosphorus pentasulfide, and 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline.
 - 4) In dip-coating tests, N,N'-di-3-(5-methylheptyl)-p-pd, N,N'-di-2-octyl-p-pd, N,N'-di-sec-butyl-p-pd, and N-butyl-p-aminophenol gave protection to SBR loops exposed

-
- (1) Eastozone 32, Eastman Chemical Co.
 - (2) Eastozone 31, Eastman Chemical Co.

to 100 pphm ozone for over seven months. Preferential reaction of ozone with these antiozonants is a suggested mechanism of the protection as distinguished from the mechanism of protection afforded by waxes (which form protective films.). The more volatile antiozonants performed generally less well in dip-coating tests (Appendix D-5). However, if the dip-coated loops had been packaged for a few weeks prior to exposure to ozone, so that the effective but comparatively volatile antiozonants were given more time in which to penetrate and/or combine with the rubber, they might have equalled or surpassed in performance the materials listed above.

- 5) The effective use of packaging antiozonants is exemplified by the photographs of Appendix E.

V. Discussion

A) Mechanism of Packaging Antiozonant Protection

Although an investigation of the mechanisms involved in the effectiveness of packaging antiozonants was not an objective of the contract, some observations on a practical level were made:

1. For most of the materials tested, there was little or no evidence of vapor phase activity in the sense of the surrounding of the rubber item with an atmosphere of ozone-destroying vapors. As a general rule, those materials which proved most effective in long-term packaging tests were those which conferred upon SBR loops packaged with them a considerable residual protection, evidently due to the formation of a coating and/or reaction with the vulcanizate. Furthermore, on the basis of published investigations of antiozonant mechanisms, it is not conclusive that ozone reacts preferentially with all the materials found to be effective in this evaluation, although such preferential reaction is undoubtedly a factor in the protection given by some of the materials tested (e.g., the Eastozones and 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline), and reaction with ozone probably occurs at least to some extent with these materials in vapor phase.

2. The residual protection provided by packaging antiozonants does not consist of a coating of the original material, as is shown in many cases by the durability of the protection given, and also by test results showing that storage after pre-exposure to antiozonant vapors (but prior to exposure to ozone) greatly increased the period of residual protection imparted by DETA and presumably by other relatively volatile materials (Appendix D-8a).

3. The more effective packaging antiozonants when used in the amount of five grams to a quart jar produce an easily visible coating on the surface of the rubber. Coatings of oxidized antiozonants may provide a degree of protection similar to that provided by wax. However, the residual protection possessed by loops thus coated (by vapor exposure) was not easily destroyed by the disturbance of these coatings -- e.g., by cracking through flexing of the brittle transparent coating produced by menthane diamine, or washing (in water and isopropanol) of the coating produced by DETA. Coatings of oxidized DETA are very resistant to solvent action and are difficult to wash off, so that results of this test may conform to the oxidized-film mechanism, but are not conclusive since the oxidized film may have residual activity for ozone.

4. Tensile tests of SBR dumbbells exposed to vapors of packaging antiozonants showed that the more effective materials tended to produce a state of overcure, but that the degree of residual protection was not proportional to the degree of overcure (Appendix D-7). For example, tetrabutyl thiourea, phosphorus pentasulfide, and piperidinium pentamethylene dithiocarbamate -- all compounds containing sulfur -- resulted in a definite overcure but did not give as much protection as did some of the aliphatic amines which showed a curing effect that ranged from insignificant to slight. That the lesser protection given by the sulfur compounds listed above was not due to excessive overcure of the surface rubber is indicated by the fact that diethyldithiocarbamic acid diethylammonium salt produced a state of overcure greater than that effected by phosphorus pentasulfide and comparable to that effected by tetrabutyl thiourea, but still afforded more protection than did either of those two materials.

These results may be partly explainable in terms of the depth of the surface overcure produced, but also basically different reactions may be involved. A surface of rubber overcured to a certain extent would be expected to show decreased susceptibility to ozone attack; but amine compounds may function in ways of which overcure is more a symptom than the primary result; i.e., they or their reaction products may not only react with free sulfur (and possibly also with bound sulfur) to effect a tighter state of cure, but in so doing may retain the more important ability to react with ozone, or even possibly that of serving as catalysts for decomposition of ozone or as negative catalysts for ozonization of rubber.

5. The residual protection provided by even the best packaging antiozonants tested is eventually lost, with failure occurring earlier at higher ozone concentrations. This suggests a gradual consumption of the antiozonant or its reaction products. The possible role of the degree of overcure of the surface rubber in the failure of "protection against ozone" requires further testing.

6. When SBR-1500 loops protected by a residual effect imparted by antiozonant vapors finally crack, the pattern of cracking is different from that of unprotected SBR-1500. In unprotected SBR loops exposed to ozone, the cracking is always general over the area of stress and the many cracks run transversely to the direction of the main stress. In "protected" loops, cracking begins at one site, or at most a comparatively few sites on the loop, and the nature of the cracking is influenced by the ozone concentration and the thickness of the rubber as discussed below.

Cracks in protected loops of about 0.020" thickness develop from the original site (more frequently on an edge) with continued growth transverse to the direction of stress, until failure of the loop occurs, sometimes from only one crack. In SBR loops of 0.085" thickness exposed to 100 pphm ozone, cracking frequently begins in a rosette pattern with a number of cracks radiating from one apparently unprotected site. However, there is little continuation of growth except in cracks more or less transverse to the direction of stress. The others soon change their course, stop growing, or run into cracks that are transverse. The "rosette" pattern of cracking is seen only in loops which have exhibited a high degree of resistance to ozone prior to the time of cracking. When highly effective packaging anti-ozonants are not given sufficient time to effect an optimum residual protection, cracking may show a pattern identical with that of unprotected rubber; or, with more pre-exposure time, a pattern similar to that of unprotected rubber except that the cracks are fewer in number and deeper.

Also, rosette cracking has not been seen to occur at low ozone concentrations. All loops that have failed in long-term packaging tests have shown a pattern of cracking very similar to that of the control loops.

7. Mild reaction of the rubber containing paraffin wax with low ozone concentrations (estimated to be less than 5 pphm) appeared beneficial. Loops of 0.020" thick SBR containing wax gained some residual protection by pre-exposure to very low concentrations of ozone at 40°C for one week (at the end of which period slight microscopic cracking had occurred). Loops so treated did not develop microscopic cracking as quickly as untreated control loops upon subsequent exposure to 100 pphm ozone.

The cracking pattern of ozone pre-treated loops was similar to that of antiozonant vapor pre-coated loops of the same thickness in that there were few microscopic cracks per loop. Little or no protection was given to wax-free SBR loops by the same pre-exposure to mild ozone, or to SBR loops containing wax by heating at 40°C for the same length of time (Appendix D-8c).

8. Pre-stressed loops in "vapor-coating" tests (Appendix D-8) showed better resistance to ozone than loops formed after "vapor-coating". These data should be supplemented but it does appear that short "vapor-coating" periods gives a surface coating that can be broken by subsequent stressing. Longer exposure may give deeper penetrating of vapors and obviate this effect of stress.

B) Correlation of Test Results

The screening test was established for the purpose of rapid indication of materials which might be especially effective as packaging antiozonants.

Results of the long term bag tests showed that the screening test served its purpose fairly well. Some materials giving complete protection in closed bags showed little or no promise in the screening tests, and these same materials failed in vented bag test. On the other hand all materials giving complete protection in the vented bag tests also completely prevented cracking in the screening test (with the exception of p-phenylenediamine, which allowed only slight cracking).

The vapor pre-coating test, originally set up to provide an indication of mechanism, actually proved to be an accurate method of evaluating packaging antiozonants. Within the limits of the testing, all antiozonants which provided residual resistance to 100 pphm ozone for a day or more, gave complete protection in vented bag or jar tests. Also the vapor pre-coating test correctly indicated that tetraethylenepentamine is a more effective packaging antiozonant than p-phenylenediamine. Both gave complete protection in the vented bag tests, but in vented jar tests which are run on the floor of the ozone box where the ozone concentration is somewhat stronger than in the bag tests, p-phenylenediamine allowed microscopic cracking in eighteen weeks, whereas the loops protected by TEPA remained uncracked for the 44 weeks duration of the test. A comparative presentation of test data on the more effective antiozonants is given in Appendix D-7.

Some mention should be made of divergent data obtained in some of the bag tests. In some cases, cracking developed more quickly in "closed" bags than in "vented" bags. In a few instances these results appeared to be due to defects in the "closed" bags, but in most cases the anomaly was probably due to non-uniform ozone concentration within the ozone cabinet. The bags were rotated at intervals to minimize this inequality, but the specimens placed in positions of higher ozone concentration at the start of the testing were at a disadvantage in that the antiozonant vapors had not yet had much time to "coat" the SBR loops. Such factors, at worst, interfered only with the accurate evaluation of the less effective materials. The inequalities of environment were not severe enough to cause cracking of loops packaged with the better antiozonants.

Also in Appendix D-7 it may be observed that 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline performed less well in packaging tests than would be predicted on the basis of screening and vapor pre-coating tests. A possible explanation for this is that its vapors are heavy and therefore were able to reach the specimens more adequately in the screening and vapor pre-coating tests, where both loops were comparatively closer to the antiozonant than was the upper loop in the packaging test.

VI Practical Considerations and Recommendations

The test results obtained on control loops (packaged without an antiozonant) in the long term bag tests showed that the 4-mil polyethylene bags provided a fair amount of protection in themselves. Several months elapsed before cracking occurred in loops thus packaged, whereas loops placed "unpackaged" in the ozone box showed general fine microscopic cracking in two hours time. The fact that the upper loop of the pair of loops in each bag cracked much sooner than the lower loop indicates that an improved type of closure would extend the period of protection given by polyethylene bags. However, Detroit Arsenal R & D personnel have stated that in many applications an air-tight closure cannot be expected. Also there is always a chance of imperfections in the bag and possibly even a very slow diffusion of ozone through the polyethylene; the use of a packaging antiozonant therefore would seem to be warranted.

Test results have shown a number of materials to be very effective as packaging antiozonants under the conditions of the tests. However, further testing should precede the selection of a particular packaging antiozonant for a particular use. Among the investigations that should be conducted are:

1. Test of the volatility of the materials considered in terms of their ability to fill the particular package to be used with vapors of sufficient concentration to give adequate protection to all surfaces of the rubber item.
2. Physical tests of SBR after long-term storage with antiozonants, to determine which materials have least effect on tensile properties, abrasion resistance, heat build-up, etc.
3. Dynamic ozone tests after long-term packaging to determine the effects of the residual protection gained by SBR during storage with antiozonants, on the life of the SBR upon use or resumption of use.
4. The choice of a particular packaging antiozonant should also of course take into consideration the method to be used in applying the antiozonant. The several different methods of application which have been used in work on this contract are listed below with some of the advantages and disadvantages of each:

- (a) Antiozonant pills enclosed in the package with the rubber item.

---This method is very convenient. Its main disadvantage lies in the unequal distribution of antiozonant in the package volume. The rubber nearest the pills will be most affected by their vapors; and, depending on the antiozonant and amount used, there may be overcure of portions and/or underprotection of others.

- (b) Dip-coating (or spraying) of rubber items before packaging.

---This method results in a consistently uniform distribution of antiozonant on the rubber item. However, it requires specialized equipment, may be hazardous due to the use of inflammable solvents and toxic antiozonants, and is stated to be objectionable (by Arsenal personnel).

- (c) Antiozonant-impregnated wrapping.

---This method provides for both a fair uniformity of distribution and convenience. A two-layered bag with the outer layer of polyethylene and inner layer of antiozonant-impregnated paper or fabric could be used. However, the commercial preparation of such wrapping material would require certain precautions, such as the avoidance of excessive oxidation during drying and in storage prior to use.

Test results have shown that some of the alkyl substituted p-phenylenediamines are especially suitable for use in dip-coatings, while other more volatile antiozonants, listed above in section IV B, are preferable for use both in pills and in impregnated wrapping material.

VII Program

The better packaging antiozonants listed in the summary were still performing satisfactorily when work was terminated by the end of the contract. These tests should be re-initiated and continued until maximum periods of protection are established.

The shorter-term testing of "pre-exposure coated" samples should be continued to establish maximum residual protection obtainable after removal of the sample from the antiozonant atmosphere.

Additional chemicals should be tested both in packaging with additives and pre-exposure to additive vapors. Additives contemplated for such tests would in part be homologues and analogues of active materials listed in the Summary herein. These newly selected additives for testing should cover the range of high and low volatilities to establish the additives of the several types having optimum activity for packaging and coating of rubber items. About 50 materials could be selected from available chemicals from present and former antiozonant work (from 1952 to 1958).

The program for a continuation of these studies also includes study of change of tensile properties of the rubber items which may occur in storage due to overcure resulting from exposure to the additives. Recommendations for packaging can be finally given on the basis of maximum protection with a minimum of overcure of the rubber.

The aerosol type spray-coating of rubber items can be investigated if desired in comparison with packaging protection. This assumes that spray-coating methods still hold some attraction to Detroit Arsenal personnel.

VIII.

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Commander, ASTIA, ATTN: TIPDR, Arlington Hall Station, Arlington 12,
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Naval Research Laboratory, Washington 25, D.C., ATTN: Code 6110

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Components & Matrls Br., Ft. Monmouth, N.J., ATTN: E. M.
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CO, ARO(D) Box CM, Duke Station, Durham, North Carolina,
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CG, Engineer R&D Lab., Matrls Br., Ft. Belvoir, Virginia,
ATTN: Phillip Mitton

Wright Air Development Center, Wright-Patterson Air Force Base,
Dayton, Ohio, ATTN: WCRTL-3

Hq, Quartermaster Res & Dev Command, Quartermaster R&D Center,
U.S. Army, Natick, Massachusetts, ATTN: Dr. J.C. Montermoso (2)

Commander Naval Ordnance Laboratory, White Oak, Maryland,
ATTN: Dr. A. Lightbody

Prosthetics Res Lab., Army Medical Center, Forest Glen, Maryland,
ATTN: Dr. Fred Leanard

A. E. Kinsey, B. F. Goodrich Company, Akron, Ohio

Armstrong Rubber Company, West Haven 6, Connecticut,
ATTN: C. M. Olson

Carlisle Tire & Rubber Co., Carlisle Corp., Carlisle, Pennsylvania,
ATTN:

Cooper Tire & Rubber Co., Findlay, Ohio, ATTN: Mr. L. Oneacre

Dayton Rubber Company, Dayton 1, Ohio, ATTN: Mr. J. Rockoff

Denman Rubber Company, P.O. Box 951, Warren, Ohio,
ATTN: Mr. H. F. Webster

Dunlop Tire & Rubber Co., Buffalo 7, New York, ATTN: Mr. H. Elden

Firestone Tire & Rubber Company, Akron 17, Ohio, ATTN: Mr. R. A.
Robertson

Gates Rubber Company, Denver, Colorado, ATTN: Mr. Lee Mitchell

General Tire & Rubber Company, Akron, Ohio, ATTN: Mr. C. W. Moss

Kelly-Springfield Tire Corp., Cumberland, Maryland,
ATTN: Mr. R. T. Bete

Lee Rubber & Tire Co., Conschohocken, Pennsylvania,
ATTN: Mr. A. H. Nellen

Mansfield Tire & Rubber Co., Mansfield, Ohio, ATTN: Mr. H. B. Partenheimer

Mohawk Rubber Co., Akron, Ohio, ATTN: Mr. R. D. Juve

McCreary Tire & Rubber Co., Indiana, Pennsylvania, ATTN: Mr. H. Reed

Frank G. Schunuit Rubber Co., Railroad & Union Avenues, Baltimore 11, Maryland, ATTN: Mr. V. V. Wheeler

Seiberling Rubber Co., Akron 9, Ohio, ATTN: Mr. O. H. Johnson

U. S. Rubber Co., 6600 E. Jefferson Avenue, Detroit 28, Mich., ATTN: Mr. W. S. McDowell

The Tire & Rim Association, Inc., Akron, Ohio, ATTN: Mr. C. N. Dykes

Burke Research Co., P.O. Box 1266, Pompano Beach, Florida, ATTN: Dr. O. W. Burke, Jr. (3)

Olin-Mathieson, High Energy Fuels Div., P.O. Box 438, Niagra Falls, New York, ATTN: Mr. William Taft

CO., DOFL, Washington 25, D.C., ATTN: ORDTL-012 (1) and Lab. 400 (1)

Commander, British Army Staff, 3100 Mass. Ave., N.W., Washington 8, D.C. (2)

Commander, Canadian Army Staff, 2450 Massachusetts Ave., N.W., Washington 8, D.C. (2)

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Chief of Research & Development, Dept. of the Army, Washington 25, D.C., ATTN: CRD/D (2)

Ord Engr Res Office, OTIA, Arlington Hall Station, Arlington 12, Virginia, ATTN: ORDLI-EO

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Appendix A

Rubber Compounds Used in Tests

All rubber compounds used in the tests were prepared by the V.L. Smithers Laboratories, Akron, Ohio, according to the following recipe, with the exception that in the first batch (used in Group I of the packaging tests) 1.5 parts of Atlantic 1115 wax was added.

<u>Ingredient</u>	<u>Pts. by Weight</u>
SBR 1500	100
HAF Black	50
Zinc Oxide	3
Stearic acid	1.5
ParaFlux 2016	3.5
Circo Light Oil	3.5
Sulfur	2.0
Santocure	1.25

The sample slabs were cured at 285° F for 45 minutes. The different batches varied slightly as to properties, but representative stress-strain values are:

Tensile, psi	3540
300% Modulus	1830
Elongation, %	515
Set at break, %	16

The cured slabs were of two approximate thicknesses. Those of about 0.020 inch thickness were used in the screening tests and some of the vapor pre-coating tests. Specimens of 0.085 inch thickness were used in the other tests. Strips of one-inch width were cut with a die for use in all tests except tensile tests. In the latter, standard-shaped dumbbells were used.

Appendix B

Ozone Exposure Tests

Ozone concentrations in the test cabinets were maintained at 100 ± 5 pphm as was determined by the method described in ASTM D-1149-55T, "Test for Accelerated Ozone Cracking of Vulcanized Rubber". Alternately, control SBR loops were placed in the boxes for a period of two hours, after which they were examined for microscopic cracking as a practical spot check on ozone concentration.

Ozone cabinet No. 1 contained the ozone generator, a quartz lamp (Model No. 693A0010, Hanovia Chemical and Manufacturing Co.). Air was circulated through and out of the first cabinet by means of a 60 c.f.m. blower. It then passed through a duct into the second cabinet and was "pulled" out of this box and passed through a wall vent with the aid of a second identical blower.

Ozone concentrations were approximately uniform throughout cabinet No. 2 which was narrow and vertical. All vapor pre-coating tests and dip-coating tests were run in Box No. 2.

Ozone concentrations were much less uniform in cabinet No. 1, and this was compensated for in various ways, such as frequent rotation of test-specimens and the avoidance of areas of the box that were known to have unusually high ozone concentrations.

Ozone cabinet No. 1 was rectangular, was made of plywood and was lined completely with aluminum. The inside dimensions were 34" (length), 18" (depth), and 26" (height). The fresh air drawn into this cabinet was passed over two strip heaters set to heat the air to 40°C . before passing over the Hanovia quartz tube. The blower rates were calculated to give 5 to 6 cabinet-volumes of air per minute. The ozonized air enters at one upper corner and leaves through the opposite lower corner.

Ozone cabinet No. 2, also rectangular, consists of an aluminum lined plywood box of the following dimensions: 64" height, 13.5" depth, and 13.5" width. The ozonized air (from box No. 1) enters via 2.5" flexible metal hose 0.5" from the bottom and is pulled therefrom by a 60 c.f.m blower mounted on the top center of the cabinet.

Appendix C

Index of Materials Tested

Material	Appendix D-No. (Table No. in Parentheses)
5-Acenapthenamine	1 (II)
2-Allyloxy-4,6-diamino-s-triazine	1 (II)
1-Allyl-2-thiourea	1 (II)
p-Aminodiphenyl	1 (II), 2 (II), 3 (I)
p-Aminodiphenylamine	1 (II), 2 (II)
Aminoguanadine bicarbonate	1 (II)
p-Aminophenol	1 (II)
2-Aminopyridine	1 (II), 3 (I)
2-Aminothiazole	1 (II), 2 (IV), 3 (I)
Ammonium caseinate	1 (II)
Anthracene	1 (II), 2 (III), 7 (I)
Armene HTD ⁽¹⁾	1 (II), 3 (III), 4 (I)
Armeen S ⁽²⁾	1 (II), 3 (I), 4 (I)
Armeen TD ⁽³⁾	3 (I), 4 (I)
Arochlor 1221 ⁽⁴⁾	1 (II)
Azobenzene	1 (II)
Bardol ⁽⁵⁾	1 (II)
Benzidine	2 (I, II)
o-Benzoic sulfimide	1 (II)
Benzonitrile	2 (II)
Benzothiazyl disulfide	3 (I)
N-n-Butyl-p-Aminophenol	5 (I)
N-sec-butyl-p-pd ⁽⁶⁾	1 (II), 3 (I), 4 (I)
2-Chlorobenzothiazole	1 (II)
Cresol	1 (II), 2 (II), 6 (I)
DAPD-215B (Akron Paint & Varnish Co.)	5 (I)
2,6-Diallyl-4-methoxyphenol	1 (II)
4,4-Diaminodiphenylamine	1 (II), 2 (II, IV)

- (1) Mixture of C16 and C18 amines, Armour Chemical Co.
- (2) "Soy Amine", Armour Chemical Co.
- (3) "Tallow Amine", Armour Chemical Co.
- (4) Chlorinated Biphenyl, Monsanto Chemical Co.
- (5) Refined coal-tar fraction, Barrett Div.
- (6) pd= phenylenediamine

Material	Appendix D-No. (Table No. in Parentheses)
p,p'-Di(aminophenyl) methane	2 (II)
2,6-Diaminopyridine	1 (II), 2 (II), 3 (I), 7 (I)
1,3-Di-n-amylthiourea	3 (I)
p,p'-Dibenzoylquinonedioxime	1 (II)
N,N'-Dibenzylthiooxamide	1 (II), 2 (II)
N,N'-Di-sec-butyl-p-pd	1 (II), 2 (II), 3 (I), 4 (I), 5 (I)
1,3-Di-sec-butylthiourea	1 (II), 2 (II), 5 (I)
p-Dichlorobenzene	1 (II)
Dicyclohexylammonium nitrite (1)	1 (II), 2 (II), 3 (I), 4 (I), 7 (I)
N,N'-Dicyclohexylthiooxamide	2 (II)
N,N'-Dicyclohexyl-p-pd	1 (II), 2 (II), 3 (I)
N,N'-Di-4(2,6-dimethyl-heptyl)-p-pd	1 (II)
Diethylthiocarbamic acid diethylammonium salt	1 (II), 3 (I), 4 (I), 7 (I),
Diethylenetriamine	2 (IV), 3 (I), 4 (I), 5 (I), 7 (I), 8
1,3-Diethylthiourea	1 (II), 2 (II, IV)
Diisopropylammonium nitrite (2)	1 (II), 2 (IV), 7 (I)
1,3-Diisopropyl-2-thiourea	1 (II)
N,N'-Dimethyl-N,N'-dioctyl-p-pd	1 (II)
N,N'-Di(1-methyl-isoamyl)-p-pd	1 (II)
Dimethylnaphthalene	1 (II)
2,5-Dimethylpiperazine	1 (II), 2 (IV), 3 (I), 4 (I), 7 (I)
2,7-Dimethylquinoline	1 (II), 2 (II), 3 (I), 4 (I), 7 (I)
N,N'-Dimethyl-N,N'-di-(1-methylpropyl)- p-pd (3)	1 (II), 2 (I,II,III), 3 (I), 4 (I), 5 (I), 6 (I,II), 7 (I)
N,N'-Di-3-(5-methyl-heptyl)-p-pd (4)	1 (II), 2 (I,II), 3 (I), 4 (I), 5 (I), 6 (I,II), 7 (I)
p-Dinitroso-benzene with inert filler (5)	3 (I)
N,N'-Di-2-octyl-p-pd (6)	1 (II), 2 (I,II), 3 (I), 5 (I)
Dithioammelide	1 (II)
Dithiooxamide	1 (II)
(1) Shell VPI-260 crystals	(4) Eastozone 31
(2) Shell VPI-220 crystals	(5) Polyac, Du Pont
(3) Eastozone 32, Eastman Chem.	(6) Eastozone 30

Appendix D-No.
(Table No. in Parentheses)

Material	
Divinyl sulfone	1 (II), 2(II)
Dodecylamine, 90% (1)	1(II), 2(IV), 3(I), 4(I), 6(I,II), 7(I)
Dodecyl-2,2,4-trimethyl-1,2-dihydroquinoline	1(II)
6-Ethoxy,2,2,4-trimethyl-1,2-dihydroquinoline	1(II), 2(II,III), 3(I), 5(I), 7(I)
Ethylenethiourea	2(II)
Reaction product, 6 moles di-(1-ethyl-3 methylpentyl)-p-pd with 1 mole phosphorus pentasulfide	1(II)
Furfurylamine	1(II), 2(III), 3(I), 4(I), 5(I), 7(I)
Hexamethylenetetramine	1(II)
Hydroquinone	1(II), 2(II), 3(I), 4(I), 6(I), 7(I)
Beta-Isopropylaminopropionitrile	1(II), 2(II), 3(I)
Ligro (tall oil)	1(II)
Menthane diamine	1(II), 2(III), 3(I), 4(I), 6(I,II), 7(I)
p-Methoxyphenol	1(II)
N-Methylaniline	1(II), 3(I)
p,p'-Methylenebis-(N,N-dimethylaniline)	1(II)
Naphthalene	1(II), 2(I), 3(I)
1-Naphthylamine	1(II), 2(III,IV), 3(I), 5(I)
1-Naphthylaminehydrochloride	1(II)
Nickel dibutyl dithiocarbamate	1(II)
Nitrobenzene	1(II)
Nitroguanidine	1(II)
Nonox HFN (2)	1(II)
Octylamine, 90% (3)	3(I)
Phenanthrene	6(I)
N-Phenyl-N'-cyclohexyl-p-pd	1(II), 2(II), 3(I)
o-Phenylenediamine	2(II), 3(I), 7(I)
m-Phenylenediamine	1(II), 2(II), 3(I), 4(I), 6(II), 7(I)
p-Phenylenediamine	1(II), 2(II,III), 3(I), 7(I)
Reaction product 3 moles p-pd, 1 mole phosphorus pentasulfide	1(II)

- (1) Armeen 12D, Armour Chemical Co.
- (2) Imperial Chemical Industries (blend of arylamines).
- (3) Armeen 8D, Armour Chemical Co.

Material	
Diethyl ether	1(II)
N-Phenyl-N'-isopropyl-p-pd	1(II), 2(II), 3(I), 7(I)
Phenyl-beta-naphthylamine	1(II)
N-Phenyl-N'-(2-octyl)-p-pd	1(II)
Phosphorus pentasulfide	1(II), 2(II,III), 3(I), 4(I), 7(I)
Piperidinium pentamethylene dithiocarbamate	1(II), 3(I), 4(I), 7(I)
Polyalkylpyridines 180 (1)	2(I)
Polyamine H Special (2)	1(II), 2(III, IV), 3(I), 4(I), 5(I), 7(I)
Polyamine T (2)	1(II)
Polygard (3)	1(II), 3(I)
Quinaldine, 60%	1(II)
Quinoline	1(II), 2(II), 3(I)
Rhodanine	1(II)
Tetrabutylthiourea	1(II), 2(III, IV), 3(I), 4(I), 5(I), 7(I)
Tetraethylenepentamine (TEPA)	1(II), 2(II), 3(I), 4(I), 5(I), 6(I,II), 7(I)
Reaction Product 1 mole TEPA and 1 mole lactonitrile	1(II)
p-Toluidine	1(II), 2(II), 3(I)
4,4',4'''-Triaminotriphenylmethane	1(II), 2(II)
Tri-tert-butyl-p-phenylphenol	3(I)
Triethanolamine	3(I), 4(I)
Triethylenetetramine	1(II), 2(IV), 3(I), 4(I), 7(I)
Triphenylmethane	1(II)
Urea	1(II), 2(II), 3(I)
2-Vinylpyridine (partially polymerized)	1(II), 3(I)
Wingstay 100 (4)	1(II), 3(I), 6(I)
Wingstay 200 (4)	6(I,II)

- (1) Reilly Tar & Chemical Co.
 (2) Union Carbide Chemicals Co.
 (3) Alkylated aryl phosphites, Naugatuck Chemical Co.
 (4) Goodyear Tire and Rubber Co.

Appendix D

Test Procedures and ResultsD-1 Screening TestsProcedure

In the screening test, two loops of SBR (approximately 0.02" in thickness) in spring-clip holders are placed side by side and upright in pint jars so that the tops of the loops are about 2-1/2 inches above the bottom of the jar. Five grams of antiozonant are placed on the bottom of the jar, and the jar opening is covered with a piece of 4-mil polyethylene in which six 5.5 mm. diameter holes have been punched. The polyethylene is held tightly in place by the ring of a standard two-piece canning closure. (The spring-clip holders employed are shown in one of the photographs of Appendix E where several of the "closed bag" samples are pictured.) The average ozone concentration based on sampling was maintained at 100 ± 5 pphm.

Because the ozone concentration is not uniform throughout the box, fifteen positions for the testing jars have been marked on the floor of the box and numbered 1-15. Jars are numbered to correspond with their position during the test, and this position is included in test data. Crack depth data obtained on control loops (without antiozonant) are shown in Table D-1-I. From these data it can be seen that the ozone concentration is much higher in position one than in the other positions. Positions 6 and 11 were reserved for controls. In some instances it seemed probable that protection was given to control loops by antiozonant vapors escaping from nearby jars.

Table D-1-I

Cracking of Control Loops in the Fifteen Positions

Used in Screening Tests with no Additives

64 Hrs. Duration; 100±5 pphm ozone; 40°C.

Position	Loop 1			Loop 2		
	Macro- scopic Cracking	No. of Cracks	Av. Crack Depth Microns	Macro- scopic Cracking	No. of Cracks	Av. Crack Depth Microns
1.	Severe	21	367	Severe	18	331
2.	Severe	21	260	Moderate	8	170
3.	Fine	6	91	Fine	16	158
4.	Moderate	21	197	Fine	12	169
5.	Fine	6	99	Moderate	22	218
6.	Fine	7	99	Fine	28	115
7.	Fine	10	127	Fine	14	90
8.	Moderate	10	139	Fine	5	121
9.	Moderate	17	180	Fine	23	141
10.	Fine	13	83	Moderate	12	133
11.	Fine	18	116	Severe	17	276
12.	Fine	13	157	Moderate	13	234
13.	Moderate	14	132	Fine	22	110
14.	Moderate	20	234	Moderate	14	163
15.	Moderate	17	204	Fine	7	83

Table D-1 - II

Screening Test Data on Antiozonants: 64 hrs. @ 100±5 pphm ozone at 40°C.

Antiozonant	Position	Macroscopic Surface Cracking	Av. Crack Depth Microns	Surface Cracking of Controls	
				Position 6	Position 11
Acenaphthenamine	7	Pronounced	-	Pronounced	Severe
		Moderate	-	Pronounced	Severe
2-Allyloxy- 4,6-diamino-s-triazine	12	Severe	-	Pronounced	Severe
		Moderate	-	Pronounced	Severe
1-Allyl -2 Thiourea	12	Slight	-	-	Severe
		Pronounced	-	-	V. Severe
p-Aminodiphenyl	13	Slight	-	Moderate	Moderate
		Moderate	-	Moderate	Pronounced
p-Aminodiphenyl-amine	12	Moderate	-	Moderate	Moderate
		Moderate	-	Moderate	Pronounced
Aminoguanidine bicarbonate	2	Severe	-	-	Pronounced
		Severe	-	-	Pronounced
p-Aminophenol	7	Slight	-	Moderate	Moderate
		Moderate	-	Moderate	Pronounced
2-Aminopyridine	12	None	0	Slight	Pronounced
		None	0	Moderate	Pronounced
2-Aminothiazole	1	None	0	-	Pronounced
		None	0	-	Pronounced
Ammonium Caseinate	7	Pronounced	-	Pronounced	V. Severe
		Pronounced	-	Pronounced	V. Severe
Anthracene	4	Fine	135	Fine	-
		Moderate	220	Moderate	-
Armeen HTD (1)	2	Slight	-	Pronounced	Pronounced
		Pronounced	-	Severe	Severe
Armeen S(1)	1	None	0	-	Pronounced
		Few pinhole cracks	None in sampling	-	Severe
Aroclor 1221(2)	13	Slight	-	Moderate	Severe
		Moderate	-	Moderate	Severe
Azobenzene	12	Slight	-	Slight	Pronounced
		Pronounced	-	Slight	Pronounced
Bardol (3)	9	Fine	-	Fine	Moderate
		Fine	-	V. Fine	Severe

(1) Amines by Armour Chemical 12D is a primary amine 90% octyl, HTD is a primary amine mixture 70% octadecyl and 25% hexadecyl. Armeen S is a "soy amine".

(2) Chlorinated biphenyl, Monsanto Chemical.

(3) Refined coat tar fraction, Barrett Div. Allied Chemical and Dye.

Table D-1 - II (Continued)

Antiozonant	Position	Macroscopic Surface Cracking	Av. Crack Depth Microns	Surface Cracking of Controls	
				Position 6	Position 11
O-Benzoin Sulfimide	1	Broke		-	Moderate
		Broke		-	Pronounced
N-sec-Butyl-p-pd.	1	None	0	None	Pronounced
		None	0	Slight	Severe
2-Chlorobenzothiazole	7	None	0	-	Moderate
		None	0	-	Pronounced
Cresol	2	Fine	-	Fine	Moderate
		Pronounced	-	V.Fine	Severe
2-6-Diallyl-4 Methoxyphenol	2	Pronounced	-	-	Severe
		Moderate	-	-	Severe
4-4-Diaminodiphenylamine	5	Slight	-	Slight	Pronounced
		Pronounced	-	Slight	Pronounced
2-6-Diaminopyridine	1	Pronounced	217	Failed	Moderate
		Pronounced	214	Failed	Pronounced
p-p'-Dibenzoylquinone-dioxime	13	Slight	-	Slight	Pronounced
		Slight	-	Slight	Pronounced
N-N' Dibenzylthioxamide	14	Moderate	-	Slight	Pronounced
		Slight	-	Moderate	Pronounced
N,N'-Di-sec-butyl-p-pd	1	None	0	-	Severe
		None	0	-	Pronounced
1,3-Di-sec-butylthiourea	2	Fine	67	Fine	-
		Moderate	175	Moderate	-
p-Dichlorobenzene	5	None	24	Fine	-
		V.Slight	48	Moderate	-
Dicyclohexylammonium nitrite	1	None	0	-	Pronounced
		None	0	-	Pronounced
N,N'-Dicyclohexyl-p-pd	8	Slight	-	Moderate	Moderate
		Moderate	-	Moderate	Pronounced
N,N'-Di-4(2,6-Dimethyl,-heptyl)-p-pd	12	Severe		Pronounced	Severe
		Failed		Pronounced	Broke
Diethyldithiocarbamic Acid diethylammonium salt	1	None	0	-	Severe
		None	0	-	V.Severe
1-3 Diethylthiourea	4	Slight	-	Moderate	Severe
		Moderate	-	Moderate	Severe
N,N'-Di(1-methyl-isoamyl)-p-pd	12	Slight		-	Moderate
		Pronounced		-	Severe
Diisopropylammonium Nitrite	1	2 severe cracks only	357	-	Severe
		1 moderate crack only	No cracks in sampling	-	Severe

Table D-1 - II (Continued)

Antiozonant	Position	Macroscopic Surface Cracking	Av. Crack Depth Microns	Surface Cracking of Controls	
				Position 6	Position 11
1,3 Di-isopropyl-2-thiourea	2	Broke Broke	- -	- -	Moderate Pronounced
Dimethyl-dioctyl-p-pd	12	Pronounced Pronounced	- -	- -	Pronounced Severe
Dimethylnaphthalene	12	Pronounced Pronounced	- -	- -	Pronounced Pronounced
2,5-Dimethylpiperazine	1	None None	0 0	- -	Severe V. Severe
2,7-Dimethylquinoline	2	None None	0 0	Pronounced Pronounced	V. Severe V. Severe
N,N'-Di-2-octyl-p-pd (1)	1	Pronounced Pronounced	175 144	- -	Pronounced Pronounced
N,N'-Di-3-(5-methylheptyl)-p-pd (2)	1	Pronounced Slight	- -	- -	Moderate Pronounced
N,N'-Dimethyl-N,N'-di(1-methyl-propyl)-p-pd (3)	2	V. Slight None	89 0	Failed Failed	Moderate Pronounced
Dithioammelide	7	Severe Severe	- -	- -	Severe V. Severe
Dithiooxamide	9	Slight V. Slight	- -	Slight Slight	Pronounced Pronounced
Divinyl sulfone	3	Slight Moderate	- -	Moderate Moderate	Moderate Pronounced
Dodecyl-2,2,4-trimethyl dihydroquinoline	1	Slight scattered	No cracks in sampling	-	Slight
		Severe	264	-	Pronounced
6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	1	None None	0 0	Fine Moderate	- -
Reaction product of 6 moles Eastozone 31(2) with 1 mole P ₂ S ₅	2	Slight Pronounced	- -	- -	Slight Slight
Furfurylamine	5	None None	0 0	Slight Moderate	Pronounced Pronounced
Hexamethylene tetramine	15	Pronounced Pronounced	- -	Slight Slight	Pronounced Pronounced
Hydroquinone	4	Moderate Severe	- -	Fine V. Fine	Moderate Severe

- (1) Eastozone 30 - Eastman Chemical Company
 (2) Eastozone 31 - Eastman Chemical Company
 (3) Eastozone 32 - Eastman Chemical Company

Table D-1 -- II (Continued)

Antiozonant	Position	Macroscopic Surface Cracking	Av. Crack Depth Microns	Surface Cracking of Controls	
				Position 6	Position 11
B-Isopropylamino-propio-nitrile	1	None	0	Pronounced	-
Ligro (tall oil)	14	Slight	-	Moderate	Severe
		Slight	-	Moderate	Severe
Menthane Diamine	1	None	0	Pronounced	Pronounced
		None	0	Pronounced	Severe
Dodecylamine, 90% (1)	1	None	0	Pronounced	V. Severe
		None	0	Pronounced	V. Severe
p-Methoxyphenol	4	Slight	-	Moderate	Moderate
		Moderate	-	Moderate	Pronounced
N-Methylaniline	1	None	0	-	Pronounced
		None	0	-	Severe
p-p'-Methylenebis (N,N-dimethylaniline)	1	Broke	-	-	Pronounced
		Broke	-	-	Severe
Naphthalene	5	Slight	-	Moderate	Moderate
		Slight	-	Moderate	Pronounced
1-Naphthylamine	1	None	0	Failed	Pronounced
		None	0	Failed	Severe
1-Naphthylamine-hydrochloride	8	None	-	None	Pronounced
		V. Slight	-	V. Slight	Pronounced
Nickel dibutyl dithio-carbonate	2	Failed	-	Moderate	V. Severe
		Failed	-	Severe	V. Severe
Nitrobenzene	15	Slight	-	Moderate	Severe
		Slight	-	Moderate	Severe
Nitroguanidine	1	Broke	-	-	Slight
		Broke	-	-	Slight
Nonox HFN (2)	1	Slight	-	-	Moderate
		Pronounced	-	-	Severe
N-Phenyl-N'-Cyclo-hexyl-p-pd	1	Slight	142	Pronounced	Slight
		Moderate	180	Severe	Pronounced
m-Phenylenediamine	1	None	0	-	Moderate
		None	0	-	Pronounced
p-Phenylenediamine	1	Fine	86	Fine	Moderate
		Fine	88	V. Fine	Severe
Reaction Product 3 moles p-pd with 1 mole phosphorus pentasulfide	1	Pronounced	No cracks in sampling	Pronounced	Moderate
		Severe	375	Pronounced	Severe
Phenyl ether	7	Slight	-	Slight	Pronounced
		Slight	-	Slight	Pronounced

(1) Armour Chemical

(2) Blend of arylamines (Imperial Chemical Industries, Ltd.)

Table D-1 - II (Continued)

Antiozonant	Position	Macroscopic Surface Cracking	Av. Crack Depth Microns	Surface Cracking of Controls	
				Position 6	Position 11
N-Phenyl-N'iso-propyl-p-pd	15	Slight Moderate	- -	Moderate Moderate	Moderate Pronounced
Phenyl-B-Naphthyl-amine	12	Moderate Moderate	- -	Moderate Moderate	Severe Severe
N-Phenyl-N'-(2-octyl)-p-pd	2	V.Severe V.Severe	- -	- -	Severe V.Severe
Phosphorus penta-sulfide	5	Fine V.Fine	- -	Fine V.Fine	Moderate Severe
Piperidinium pentamethylene dithiocarbamate	1	Slight Pronounced	- -	- -	Moderate Severe
Polyamine H Special (1)	1	None None	0 0	Slight Moderate	Pronounced Pronounced
Polyamine T (1)	4	Slight Slight	- -	Slight Slight	Pronounced Pronounced
Polygard (2)	1	Moderate Pronounced	119 240	Moderate Moderate	Moderate Pronounced
Quinoline	13	Fine Fine	- -	Fine V.Fine	Moderate Severe
Quinaldine	2	Moderate Moderate	- -	Slight Moderate	Pronounced Pronounced
Rhodanine	7	Pronounced Severe	- -	None Slight	Pronounced Severe
Tetrabutyl Thiourea	1	None None	0 0	Severe Moderate	V.Severe V.Severe
Tetraethylene pentamine	1	None None	0 0	Moderate Moderate	Severe Severe
Reaction product 1 mole TEPA, 1 mole lactonitrile	7	Moderate Slight	- -	Moderate Moderate	Severe Severe
p-Toluidine	15	None None	0 0	Fine V.Fine	Moderate Severe
4,4',4" Triaminotri-phenyl methane	10	Moderate Slight	- -	Moderate Moderate	Moderate Pronounced
Triethylene tetramine	1	None None	0 0	Failed V.Severe	Pronounced V.Severe
Triphenyl methane	8	Moderate Severe	- -	Moderate Moderate	Severe Severe
Urea	8	Fine Pronounced	- -	Fine V.Fine	Moderate Severe

(1) Union Carbide Chemicals

(2) Alkylated aryl phosphites - Naugatuck Chemical

Table D-1 - II (Continued)

Antiozonant	Position	Macroscopic Surface Cracking	Av. Crack Depth Microns	Surface Cracking of Controls	
				Position 6	Position 11
2-Vinyl pyridine (partially polymerized)	14	None	0	Moderate	Moderate
		None	0	Moderate	Pronounced
Wingstay 100 (1)	2	Moderate	-	Pronounced	Pronounced
		Severe	-	Pronounced	Severe

(1) Goodyear Chemical Division

Appendix D-2

Long and Intermediate Term Packaging TestsProcedure

In all of the packaging tests, the antiozonant was pilled by use of a Parr pellet press. One gram of antiozonant was used, and Suprex clay was combined with antiozonants which could not be pilled alone.

The 4-mil polyethylene bags used in the packaging tests were made at the Burke Research Company, and were approximately four by eight inches in size.

Two SBR loops were enclosed in each bag (or jar) and were held in a metal clip in such a way that one loop was above the other, and thus farther from the antiozonant at the bottom of the bag (or jar) and closer to the bag's closure.

In the "closed bag" test, the neck of the bag was drawn closed around a short section of glass rod, and fastened with plastic-coated wire. This simulated closure around the tire and axle of a military vehicle, and was intended to be fairly reproducible but not air-tight (i.e., not hermetically sealed).

The "vented bag" test was identical with the closed bag test except that 4-mm I.D. glass tubing was substituted for the glass rod.

One of the photographs of Appendix E illustrates the "bag test" assembly employing the aluminum spring-clip mounting method.

In the vented jar test, the loops and antiozonant pills were enclosed in a pint jar, the mouth of which was covered with a sheet of four-mil polyethylene in which was punched one four mm. hole. The polyethylene was held in place by the ring of a standard 2-piece canning closure.

All packaging tests were conducted in an ozone cabinet maintained at 100 ± 5 pphm ozone and about 40°C .

Table D-2-ILong and Intermediate Term Packaging Tests

Group I - Closed Bag, 59 Weeks Duration, Samples of SBR-1500 with Wax, 40°C., 100±5 pphm ozone.

(Plus sign indicates specimen still uncracked at last examination.)

<u>Antiozonant</u>	<u>Parts Suprex Clay</u>	<u>Weeks to Microscopic Cracking</u>		<u>Weeks to Macroscopic Cracking</u>	
		<u>Loop 1</u>	<u>Loop 2</u>	<u>Loop 1</u>	<u>Loop 2</u>
None (control)	-	9	9	29	29
Benzidine	0	9	23	31	31
N,N'-Dimethyl-N,N'-di- (1-methylpropyl)-p-pd	4	58+	59+	59+	59+
N,N'-Di-3-(5-methylheptyl)-p-pd	4	16	16	23	27
N,N'-Di-2-octyl-p-pd	4	16	31	34	59+
Naphthalene	0				
Polyalkylpyridines 180 (Reilly Tar & Chem. Co.)	4	19	23	59+	59+

Table D-2-II

Long and Intermediate Term Packaging Tests. Group II - 54 weeks duration, samples of SBR-1500 without wax. Plus sign indicates specimen free of cracks (either microscopic or macroscopic as indicated) at last examination or at termination of test.

Antiozonant	Parts Suprex Clay	Closed Bag				Vented Bag				Appearance of Bags After 54 Weeks	Apparent Condition of Pills After 54 Weeks
		Weeks to Microscopic Cracking		Weeks to Macroscopic Cracking		Weeks to Microscopic Cracking		Weeks to Macroscopic Cracking			
		Upper Loop	Lower Loop	Upper Loop	Lower Loop	Upper Loop	Lower Loop	Upper Loop	Lower Loop		
		Loop	Loop	Loop	Loop	Loop	Loop	Loop	Loop		
p-Aminodiphenyl	0	44	54+	54+	54+	12	54+	14	54+	Brown coating on most of bag, darker at bottom	Intact
p-Aminodiphenyl-amine	0	12	54+	18	54+	12	54+	18	54+	Dense dark coating lower 1 1/2"	Intact
Anthracene	0	54+	54+	54+	54+	14	18	16	29+	No visible coating	Some-what crumbled
Benzidine	0	-	-	-	-	12	54+	16	54+	Light brown coating 2/3 of bag	Crumbled
Benzonitrile	4	24	54+	54+	54+	12	24	14	29+	No coating other than powder	Crumbled
Cresol	4	16	54+	20	54+	12	54+	14	54+	No coating other than powder	Crumbled
4,4-Diaminodiphenylamine	0	<12	<12	12	12	12	20	14	24	Discontinued previously	Intact
p-p'-Di(Amino-phenyl)methane	2	14	54+	18	54+	12	12	16	29+	Definite coating lower bag only	Intact
2,6-Diaminopyridine	0	54+	54+	54+	54+	22	54+	54+	54+	Brown coating v. dark at bottom, v. light at top	Intact
N,N'-Dibenzylthiooxamide	0	22	54+	44	54+	12	54+	14	54+	No coating	Sl. crumbled
N,N'-Di-sec-butyl-p-pd	4	36	54+	44	54+	24	54+	54+	54+	Dense dark brown coating lower 1 1/2"	Intact

Table D-2-II (Continued)

Antiozonant	Parts Suprex Clay	Closed Bag				Vented Bag				Appearance of Bags After 54 Weeks	Apparent Condition of Pills After 54 Weeks
		Weeks to Microscopic Cracking		Weeks to Macroscopic Cracking		Weeks to Microscopic Cracking		Weeks to Macroscopic Cracking			
		Upper Loop	Lower Loop	Upper Loop	Lower Loop	Upper Loop	Lower Loop	Upper Loop	Lower Loop		
1,3-Di-sec-butylthiourea	0	18	54+	20	54+	12	54+	18	54+	No apparent coating	Intact
Dicyclohexylammonium nitrite	0	-	-	-	-	54+	54+	54+	54+	Yellow coating lower 2/3	Sl. crumbled
N,N'-Dicyclohexyl-dithiooxamide	0	12	16+	16+	16+	12	16+	14	16+	Discontinued previously	
N,N'-Dicyclohexyl-p-pd	0	24	54+	54+	54+	24	54+	39	54+	Dense coating very bottom of bag only	Sl. crumbled
1,3-Diethylthiourea	0	12	29	16	54+	16	54+	22	54+	No apparent discoloration of bag	Intact
2,7-Dimethylquinoline	4	54+	54+	54+	54+	12	24	14	26+	No coating except powder	Sl. crumbled
N,N'-Dimethyl-N,N'-di(1-methylpropyl)-p-pd	4	54+	54+	54+	54+	34	54+	36	54+	Thick dark coating oozing thru bag lower 1 1/2" only	Intact
N,N'-Di-3-(5-methylheptyl)p-pd	4	54+	54+	54+	54+	12	18	20	29+	Little or no discoloration	Intact
N,N'-Di-2-octyl-p-pd	4	12	24	16	29+	12	44	14	54+	Little or no discoloration	Intact
Divinyl sulfone	4	16	34	20	54+	12	54+	18	54+	No apparent coating	Sl. crumbled
6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	4	54+	54+	54+	54+	12	54+	16	54+	Some coating toward bottom of bag	Intact
Ethylenethiourea	0	-	-	-	-	16	54	20	54+	Little or no discoloration	Intact
Hydroquinone	0	54+	54+	54+	54+	12	54+	18	54+	Very light brown coating most of bag	Crumbled

Table D-2-II (Continued)

Antiozonant	Parts Suprex Clay	Closed Bag				Vented Bag				Appearance of Bags After 54 Weeks	Apparent Condition of Pills After 54 Weeks
		Weeks to		Weeks to		Weeks to		Weeks to			
		Macroscopic Cracking		Macroscopic Cracking		Macroscopic Cracking		Macroscopic Cracking			
		Upper Loop	Lower Loop	Upper Loop	Lower Loop	Upper Loop	Lower Loop	Upper Loop	Lower Loop		
β -Isopropylamino- propionitrile	4	18	34	24	54+	16	44	16	54+	No coating except powder	Crumbled
N-Phenyl-N'-cyclo- hexyl-p-pd	0	16	16	26	26	12	54	16	54	Light brown coating, most of bag	Sl. crumbled
o-Phenylenediamine	0	54+	54+	54+	54+	54+	54+	54+	54+	Dark brown coating, denser at bottom of bag	Sl. c crumbled
m-Phenylenediamine	2	54+	54+	54+	54+	54+	54+	54+	54+	" "	Intact
p-Phenylenediamine	0	54+	54+	54+	54+	54+	54+	54+	54+	Dense dark brown coating, entire bag	V. sl. crumbled
N-Phenyl-N'-iso- propyl-p-pd	0	54+	54+	54+	54+	12	54+	18	54+	Dense dark coating lower inch only	Intact
Phosphorus penta- sulfide	0	54+	54+	54+	54+	18	54+	34	54+	Irregular patches of black dis- coloration.	Soft and partly disinte- grated
Quinoline	4	16	54+	24	54+	12	54+	20	54+	No apparent coating	Crumbled
Tetraethylene pentamine	4	54+	54+	54+	54+	54+	54+	54+	54+	Yellow coating entire bag, oozing thru poly- ethylene.	Intact
p-Toluidine	0	14	18	16	20	18	18	20	20	Discontinued previously	(Dis- appeared <3 week)

Table D-2-II (Concluded)

Antiozonant	Closed Bag						Vented Bag						Appearance of Bags After 54 Weeks	Apparent Condition of Pills After 54 Weeks
	Parts Suprex Clay	Weeks to		Weeks to		Weeks to		Weeks to		Weeks to				
		Macroscopic Cracking	Upper Loop	Lower Loop	Macroscopic Cracking	Upper Loop	Lower Loop	Macroscopic Cracking	Upper Loop	Lower Loop				
4,4',4" Triamino- triphenylmethane	0	26	34	44	54+	12	<14	14	14	14	No coating other than powder	Sl. crumbled		
Urea	0	29	54+	39	54+	12	14	14	18		No apparent coating	Intact		
Control (Closed bag)	-	<16	34	16	44	-	-	-	-					
Control (Vented bag)	-	-	-	-	-	12	54+	16	54+					
Control (Vented bag)	-	-	-	-	-	12	34	16	54+					

Table D-2-III

Long and Intermediate Term Packaging Tests

Group III - SBR 1500 Without Wax - Vented Pint Jars
Ozone @ 100±5 pphm and 40°C.

Plus sign indicates specimens uncracked at termination
of test.

Antiozonant	Parts Suprex Clay	Weeks to Microscopic Cracking		Weeks to Macroscopic Cracking	
		Upper Loop	Lower Loop	Upper Loop	Lower Loop
None (control)	-	< 9	< 9	9	9
N,N'-Dimethyl-N,N'-di- (1-methylpropyl)-p-pd	4	9	44+	26	44+
6-Ethoxy-2,2,4-trimethyl- 1,2-dihydroquinoline	4	14	44+	29	44+
Furfurylamine	4	44+	44+	44+	44+
Beta-Isopropylaminopropio- nitrile	4	< 9	< 18	9	18
Menthane diamine	4	44+	44+	44+	44+
1-Naphthylamine	0	9	44+	10	44+
p-Phenylenediamine	0	18	44+	44+	44+
Phosphorus pentasulfide	1	< 9	< 9	9	9
Polyamine H Special (1)	4	44+	44+	44+	44+
Tetrabutyl thiourea	1	44+	44+	44+	44+

(1) Union Carbide Chemicals

Table D-2 - IVLong and Intermediate Term Packaging Tests

SBR 1500 samples without wax. Ozone at 100±5 pphm and 40°C.

Plus sign indicates specimen still uncracked at last examination.

Group IV - Closed Polyethylene Bags

Antiozonant	Parts Suprex Clay	Weeks to Microscopic Cracking		Weeks to Macroscopic Cracking	
		Upper Loop	Lower Loop	Upper Loop	Lower Loop
None, (control)	-	19	39+	39	39+
4,4-Diaminodiphenyl amine	0	19	39+	23	39+
1,3-Diethylthiourea	4	<31	<31	31	31
1-Naphthylamine	0	39+	39+	39+	39+
Polyamine H Special	4	39+	39+	39+	39+
Tetrabutyl thiourea	1	39+	39+	39+	39+
Triethylene tetramine	4	39+	39+	39+	39+

Group V - Vented Polyethylene Bags

Antiozonant	Parts Suprex Clay	Weeks to Microscopic Cracking		Weeks to Macroscopic Cracking	
		Upper Loop	Lower Loop	Upper Loop	Lower Loop
None (control)	-	13	27	27	27+
2-Aminothiazole	0	<13	25+	13	25+
Diethylene triamine	5	27+	27+	27+	27+
Diisopropylammonium nitrite ⁽²⁾	0	27+	27+	27+	27+
2,5-Dimethyl piperazine, trans	0	27+	27+	27+	27+
Dodecylamine, 90%	5	25+	25+	25+	25+

(1) Armeen 12D, Armour Chemical Co.

(2) Shell VPI - 220 Crystals, Shell Oil Co.

Appendix D-3

"Vapor Pre-Coating" TestsProcedure

SBR loops, in metal holders were enclosed with variable amounts of antiozonant in either pint or quart jars and for variable periods of time, at either room temperature or 40°C. In this test the antiozonant was usually not piled, but simply placed on the bottom of the jar. At the end of this period of exposure to antiozonant vapors, the rubber loops were removed from the jar and, still in their holders, were exposed directly to ozone at either 100 or about 10 ppm. (The latter concentration was found to exist on a shelf in the room in which the ozone cabinet was situated.) Occasionally the loops, after exposure to antiozonant vapors, received an additional conditioning treatment before exposure to ozone. This conditioning consisted of storage on a shelf or in a clean, closed jar.

The spring-clips for mounting of duplicate rubber loops are shown in a photograph of Appendix E.

Table D-3 - I
 "Vapor Pre-Coating" Tests: 40°C. for 100 pphm ozone and about 28°C. (r.t.) for 10 pphm.
 Plus sign indicates specimen still uncracked at termination of contract.

Antiozonant and Amount	Thickness of SBR	Jar	Exposure	Post Exposure Treatment	O ₃ pphm	Days to Macroscopic Cracking	
						Loop 1	Loop 2
None, (Control)	.020				<10	5-7	5-7
None, (Control)	.085				100	<2 hrs	<2 hrs
p-Aminodiphenyl, 5g	.085	pint	30 days r.t.	none	100	<1	<1
2-Aminopyridine, 5g	.020	pint	64 hrs, 40°C	none	10	30	-
2-Aminothiazole, 5g	.085	pint	6 days 40°C	none	100	40	-
Armeen HTD, 5g	.020	pint	5 days 40°C	none	100	<1	-
Armeen HTD, 5g	.085	quart	30 days r.t.	none	100	<1	1
Armeen S, 5g	.085	quart	30 days r.t.	none	100	<1	<1
Armeen TD, 5g	.085	quart	30 days r.t.	none	100	<1	<1
1,3-Di-n-Amylthiourea, 5g	.085	pint	6 days 40°C	none	100	<1	-
Benzothiazyl disulfide, 5g	.085	pint	30 days r.t.	none	100	<1	<1
N-sec-butyl-p-pd, 5g	.085	quart	30 days r.t.	none	100	<1	15
2,6-Diaminopyridine, 5g	.020	pint	63 hrs 40°C	none	<10	8	8
2,6-Diaminopyridine, 5g	.085	pint	30 days r.t.	none	100	<1	<1
N,N'-Di-sec-butyl-p-pd, 5g	.020	pint	64 hrs 40°C	4 days shelf r.t.	<10	25	25
N,N'-Di-sec-butyl-p-pd, 5g	.085	quart	30 days r.t.	none	100	<1	<1
Dicyclohexylammonium nitrite, 5g	.085	quart	30 days r.t.	4 days shelf r.t.	100	<1	<1
N,N'-Dicyclohexyl-p-pd, 5g	.020	pint	63 hrs 40°C	none	<10	8	8
Diethyldithiocarbamic acid diethylammonium salt	.085	quart	30 days r.t.	none	100	34+	34+
Diethylenetriamine, 5g	.085	pint	42.5 hrs r.t.	none	100	43	57
Diethylenetriamine, 4g	.085	pint	10 days r.t.	none	100	101	101
Diethylenetriamine, 3g	.085	pint	10 days r.t.	none	100	54	213
Diethylenetriamine, 2g	.085	pint	10 days r.t.	none	100	54	54
Diethylenetriamine, 1g	.085	pint	10 days r.t.	none	100	25	53
Diethylenetriamine, 5g	.085	quart	30 days r.t.	none	100	59+	59+
Diethylenetriamine, 3g	.085	quart	30 days r.t.	none	100	59+	59+
N,N'-Dimethyl - N,N'-di(1-methyl-propyl)-p-pd, 5g	.085	quart	30 days r.t.	4 days shelf r.t.	100	<1	<1
N,N'-Dimethyl-N,N'-di(1-methyl-propyl)-p-pd, 5g	.020	pint	64 hrs 40°C	none	<10	17	37

Table D-3-I (Continued)

Antiozonant and Amount	Thick- ness of SBR	Jar	Exposure	Post Ex- posure Treatment	O ₃ pphm	Days to Macroscopic Cracking	
						Loop 1	Loop 2
N,N'-Di-3-(5-methyl-heptyl)-p- pd, 5g	.020	pint	64 hrs 40°C	none	<10	16	18
N,N'-Di-2-octyl-p-pd, 5g	.020	pint	64 hrs 40°C	none	<10	9	17
2, 5-Dimethylpiperazine, 5g	.020	pint	64 hrs 40°C	none	<10	70+	70+
2, 5-Dimethylpiperazine, 5g	.085	quart	30 days r.t.	none	100	<1	<1
2, 7-Dimethylquinoline, 5g	.085	quart	30 days r.t.	none	100	<1	<1
Dodecylamine, 90%, 5g	.020	pint	5 days 40°C	none	100	202+	-
Dodecylamine, 90%, 5g	.085	quart	30 days r.t.	none	100	<1	60
6-Ethoxy-2,2,4-trimethyl-1,2- dihydroquinoline, 5g	.020	pint	64 hrs 40°C	none	<10	136+	136+
Furfurylamine, 5g	.020	pint	64 hrs 40°C	none	<10	136+	136+
Furfurylamine, 5g	.020	pint	7 days r.t.	none	<10	77+	77+
Furfurylamine, 5g	.085	pint	24 hrs 40°C	24 days shelf r.t.	100	3	108
Furfurylamine, 5g	.085	pint	24 hrs 40°C	24 days clean	100	>144	>144
Furfurylamine, 5g	.085	quart	30 days r.t.	jar r.t.	100	94+	94+
Hydroquinone	.085	quart	30 days r.t.	none	100	<1	<1
B-Isopropylaminopropionitrile, 5g	.020	pint	64 hrs 40°C	none	<10	24	24
B-Isopropylaminopropionitrile, 5g	.020	pint	7 days r.t.	none	<10	77	77+
Menthane diamine, 5g	.020	pint	64 hrs 40°C	none	<10	136+	136+
Menthane diamine, 5g	.020	pint	42.5 hrs r.t.	none	100	<1	<1
Menthane diamine, 5g	.085	quart	30 days r.t.	none	100	94+	94+
N-Methylaniline, 5g	.020	pint	64 hrs 40°C	none	<10	25	25
Naphthalene, 5g	.020	pint	64 hrs 40°C	none	<10	6	6
1-Naphthylamine 5g	.020	pint	64 hrs 40°C	none	<10	32	37
1-Naphthylamine 5g	.085	quart	30 days r.t.	none	100	<1	<1
Octylamine, 90%, 5g	.085	pint	6 days 40°C	none	100	41	-
N-Phenyl-N'-cyclohexyl-p-pd, 5g	.020	pint	64 hrs 40°C	none	<10	17	25
o-Phenylenediamine, 5g	.020	pint	64 hrs 40°C	none	<10	31	31
m-Phenylenediamine, 5g	.020	pint	64 hrs 40°C	4 days shelf r.t.	<10	31	32
m-Phenylenediamine, 5g	.085	quart	30 days r.t.	none	100	<1	<1
p-Phenylenediamine	.020	pint	64 hrs 40°C	none	<10	31	32
Phosphorus pentasulfide, 5g	.020	pint	64 hrs 40°C	none	<10	70+	70+
Phosphorus pentasulfide, 5g	.085	quart	30 days r.t.	none	100	<1	<1
N-Phenyl-N'-Isopropyl-p-pd, 5g	.020	pint	64 hrs 40°C	none	<10	11	11

Table D-3-I (Continued)

Antiozonant and Amount	Thick- ness SBR	Size Jar	Exposure	Post Ex- posure Treatment	C ₃ pphm	Days to Macroscopic Cracking	
						Loop 1	Loop 2
Piperidiniumpentamethylene- dithiocarbamate, 5g	.085	quart	30 days r.t.	none	100	2	6
Polyac *	.085	pint	8 days 40°C	none	100	1	1
Polyamine H Special 5g	.020	pint	64 hrs 40°C	none	<10	136+	136+
Polyamine H Special 5g	.085	quart	30 days r.t.	none	100	5	55
Polyamine H Special 5g	.085	pint	42.5 hrs r.t.	none	100	<1	4
Polygard, 5g	.085	pint	30 days r.t.	none	100	<1	<1
Quinoline, 5g	.020	pint	64 hrs 40°C	none	<10	6	9
Tetrabutylthiourea, 5g	.020	pint	64 hrs 40°C	none	<10	70+	70+
Tetrabutylthiourea, 5g	.085	quart	30 days r.t.	7 days shelf r.t.	100	14	14
Tetraethylenepentamine, 5g	.020	pint	64 hrs 40°C	none	<10	136+	136+
Tetraethylenepentamine, 5g	.085	quart	30 days r.t.	none	100	24	55
Tetraethylenepentamine, 5g	.020	pint	42.5 hrs r.t.	none	100	<1	<1
p-Toluidine, 5g	.020	pint	64 hrs 40°C	none	<10	17	17
Tri-tert-butyl-p-phenylphenol, 5g	.085	pint	4 days 40°C	none	100	<1	-
Triethanolamine, 5g	.020	pint	2 days 40°C	none	100	202+	-
Triethanolamine, 5g	.085	quart	30 days r.t.	none	100	<1	<1
Triethylenetetramine 5g	.085	quart	30 days r.t.	none	100	42	50+
Triethylenetetramine 5g	.020	pint	64 hrs 40°C	none	<10	136+	136+
Triethylenetetramine 5g	.085	pint	42.5 hrs r.t.	none	100	<1	<1
Urea, 5g	.085	pint	30 days r.t.	none	100	<1	<1
2-Vinylpyridine (partially poly- merized), 5 g	.020	pint	64 hrs 40°C	none	<10	21	21
Wingstay 100	.085	pint	30 days r.t.	none	100	<1	<1

* p-Dinitrosobenzene with inert filler, DuPont

Appendix D-4

Effect of Exposure to Antiozonant Vapors on
Tensile Properties of SBR-1500

Procedure: Three SBR dumbbells were enclosed with five grams of antiozonant in a quart jar, the dumbbells being suspended from near the top of the jar. After thirty days, the dumbbells were removed from the jar and tensile values were obtained. The figures below are averages of the values for three dumbbells.

Table D-4-I
Stress-Strain Data

Group	Antiozonant	Shore A Durometer	Tensile, psi	Elongation %	Modulus 300%, psi
I	Tetrabutyl thiourea	70-68	2153	250	--
	Eastozone 32	68-66	3430	510	1970
	N,N'-Di-sec-butyl-p-pd.	68-66	3233	510	1860
	m-Phenylenediamine	68-66	3233	500	1900
	Dicyclohexyl ammonium nitrite	67-65	3460	530	1890
	None (control)	69-67	3270	510	1880
II	Phosphorus pentasulfide	67-65	3410	460	2070
	2,5-Dimethylpiperazine	63-61	3690	620	1610
	Dodecylamine	62-60	3600	570	1640
	2,7-Dimethylquinoline	63-62	3570	540	1790
	Hydroquinone	65-63	3720	550	1780
	Furfurylamine	64-62	2490	480	1450
	Menthane diamine	65-63	3750	600	1720
	None (control)	64-62	3670	570	1600
III	Piperidinium penta- methylenedithiocarbamate	69-68	1898	200	
	Diethyldithiocarbamic acid diethylammonium salt	70-69	1945	293	-
	N-sec-butyl-p-pd	65-64	3440	520	1953
	Armeen HTD	65-64	3763	540	1880
	Armeen S	65-64	3450	500	1873
	Armeen TD	65-64	3450	500	1873
	None (control)	66-64	3730	513	1888
IV	Triethanolamine	68-66	3640	490	2055
	Tetraethylenepentamine	67-65	3480	485	2010
	Triethylenetetramine	64-62	3440	480	2060
	Polyamine H Special	68-66	3450	485	1940
	Diethylenetriamine, 5 g.	-	2970	425	2190
	Diethylenetriamine, 3 g.	-	3180	460	2170
	Eastozone 31(dip- coating) (1)	66-64	3420	495	1905
	None (control)	66-64	3480	480	1940
	Diethylenetriamine, 1 g. (2)	70-69	3490	470	2260
V	None (control)	69-67	3270	510	1880

- (1) Dumbbells dipped into 50% solution of Eastozone 31 in acetone and allowed to drip dry for thirty minutes before enclosure in jar.
- (2) One gram DETA was pillled with five parts Suprex clay, and enclosed with SBR dumbbells for fourteen weeks.

Appendix D-5

Dip-Coating TestsTable D-5-I

Antiozonant Coatings Applied to SBR-1500 Loops by Dipping
and Directly Exposed to 100±5 pphm ozone at 40°C.

(Numbers in parentheses indicate parts by weight in solution. Plus sign indicates test discontinued with specimen uncracked.)

Coating Solution	Days to Macroscopic Cracking
N-Butyl-p-aminophenol (50), methanol (20), isopropanol (30)*	215+
DAPD-215B Coating ***	1,1,21,23
N,N'-Di-sec-butyl-p-pd (50), Isopropanol (50)	48
N,N'-Di-sec-butyl-p-pd (50), Toluene (50)	239+
1,3-Di-sec-butylthiourea (50), Isopropanol (50), Triton X-100 (1) ***	24
Diethylene triamine (15), Water (10), Casein (2), heated to dissolve	22, 22
Diethylene triamine (1), Water (1), (Mixture of 81.5 pts. water, 3 pts. Triton X-100, 0.5 pts. hydroxyethyl cellulose) (1)	11, 22
N,N'-Dimethyl-N,N'-di-(1-methylpropyl)-p-pd (50), Isopropanol (50)	22
N,N'-Dimethyl-N,N'-di(1-methylpropyl)p-pd (50), toluene (50)	11
N,N'-Di-3-(5-methyl-heptyl)-p-pd (50), toluene (50)	239
N,N'-Di-3-(5-methyl-heptyl)p-pd, undiluted	239
N,N'-Di-2-octyl-p-pd (50), toluene (50)	239
6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (1), Isopropanol (2)	23
Furfurylamine (50), Isopropanol (50)	<1
1-Naphthylamine (50), Isopropanol (50)	<1
Polyamine H Special (50), Isopropanol (50)	21
Polyamine H Special (50), Water (50)	8, 35
Tetrabutyl thiourea (10), Isopropanol (11) Triton X-100 (0.2)	6
Tetrabutyl thiourea (1), Toluene (2)	<1
Tetrabutyl thiourea (1), Acetone (2)	<1
Tetraethylene pentamine (10), Water (15.5), 37% Formaldehyde (4.5), Triton X-100 (0.2)	45

*** Gasline Antioxidant No. 5, DuPont

** Formula LR 1588, Akron Paint & Varnish Company

*** Alkylaryl polyether alcohol, Rohm & Haas

Table D-6-I

Antiozonants Applied by Covering SBR-1500 Loops with
Cheesecloth Impregnated with Antiozonant

Method: A ten inch square of single-layer cheesecloth was soaked in a solution of 1 g. antiozonant in 9 g. solvent until all of the solution was absorbed. The cloth was suspended until thoroughly dry and then was draped over a metal holder containing 2 SBR loops. The "draped" loops were placed in a pint jar covered with 4-mil polyethylene punched with six 5.5 mm. holes, and placed in 100±5 pphm ozone box.

Plus sign indicates loops uncracked at termination of test.

Antiozonant (1 g.)	Solvent, 9 g.	Days to Macroscopic Cracking, Upper Loop
Cresol	Acetone	5
N,N'-Dimethyl-N,N'-di- (1-methylpropyl)-p-pd	Acetone	28+
N,N'-Di-3-(5-methyl-heptyl)-p-pd	Acetone	28+
Dodecylamine, 90%	Isopropanol	28+
Hydroquinone	Isopropanol	4
Menthane diamine	Acetone	28+
Phenanthrene	Toluene	4
m-Phenylenediamine	Acetone	18+
Tetraethylenepentamine	Isopropanol	28+
Wingstay 100	Acetone	5
Wingstay 200	Acetone	18+
None (control I)		4
None (control II)		4

In these tests none of the lower loops had cracked in the times shown for cracking of the upper loops.

Table D-6-II

Direct exposure of Surviving Loops of Table D-6-I
to 100±5 pphm Ozone at 40°C.

<u>Antiozonant</u>	<u>Days Pre-exposure to Antiozonant</u>	<u>Days to Macroscopic Cracking</u>
N,N'-Dimethyl-N,N'-di(1-methyl- propyl)-p-pd	28	<1, both loops
N,N'-Di-3-(5-methyl-heptyl)-p-pd	28	<1, both loops
Dodecylamine, 90%	28	<1, both loops
Menthane diamine	28	<1, both loops
m-Phenylenediamine	14	8+, both loops
Tetraethylenepentamine	28	8+, both loops
Wingstay 200	14	<1, both loops

Appendix D-7

TABLE D-7-1

Comparative Data on More Effective Materials by Several Methods of Test

In Screening Tests, A= no cracking, (position 1); B= sl. cracking, (position 1); C= somewhat less cracking than controls, (position 1); D= cracking similar to or worse than controls, (position 1). Times given are periods to macroscopic cracking. Plus sign indicates specimen uncracked at last observation.

Antiozonant	Screening Test	Packaging Tests,		Vapor Pre-Coating Test		Effect of Vapors on Tensile Properties,	
		Wks. to cracking of Upper Loop		Days to Cracking		% of control	
		Vented Bags or jars	Closed Bags	10 pphm	100 pphm	Modulus (300%)	Tensile
Diethylenetriamine	-	27+	-	-	51+(both)	115	89
Menthane diamine	A	44+	-	136+(both)	94+(both)	117	105
Furfurylamine	A	44+	-	136+(both)	94+(both)	91	84
Dimethyldithiocarbamic acid diethylammonium salt	A	-	-	-	35+(both)	-	57
Polyamine H Special	A	44+	-	136+(both)	5,51+	100	101
Triethylenetetramine	A	-	39+	136+(both)	42,51+	106	100
Tetraethylenepentamine	A	54+	54+	136+(both)	24,51+	104	101
Tetrabutyl thiourea	A	44+	39+	70+(both)	14(both)	-	49
Dodecylamine, (90% purity)	A	25+	-	-	<1,60	103	100
Piperidinium pentamethylene diethiocarbamate	-	-	-	-	6, 11	-	39
Dicyclohexylammonium nitrite	A	54+	-	-	<1(both)	101	104
2,5-Dimethyl piperazine	A	27+	-	70+(both)	<1(both)	101	109
m-phenylenediamine	A	54+	54+	31, 32	<1(both)	101	98
o-phenylenediamine	-	54+	54+	31, 32	-	-	-
p-phenylenediamine	B	54+	54+	31, 32	-	-	-
Diisopropylammonium nitrite	B	27+	-	-	-	-	-
6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	A	29	54+	136+(both)	-	-	-
Phosphorus pentasulfide	C	34	54+	70+(both)	<1(both)	129	81
N,N'-Dimethyl-N,N'-di-(1-methylpropyl)-p-pd	B	36	54+	17, 37	<1(both)	104	100
N,N'-Di-3-(5-methylheptyl)p-pd	D	20	54+	16, 18	-	-	-
N-Phenyl-N'-Isopropyl-p-pd	C	18	54+	11(both)	-	-	-
2,6-Diaminopyridine	B	16	54+	8 (both)	<1(both)	-	-
2,7-Dimethylquinoline	B	14	54+	-	<1(both)	112	95
Hydroquinone	D	18	54+	-	<1(both)	111	97
Anthracene	D	16	54+	-	-	-	-
Control	D	12-16	16-39	5-7	0.08	100	100

D-53

Appendix D-8

Miscellaneous Tests Relating To Mechanism of Protection by Packaging Antiozonants.a) Effect of Storage of "Vapor-coated" SBR-1500 Loops Prior to Exposure to Ozone

Method: Three pairs of SBR loops were enclosed in a jar with one gram of DETA for twenty-four hours. At the end of this period, the three pairs of loops were removed from the jar and stored for varying periods of time in an ozone-free atmosphere before direct exposure to 100 pphm ozone.

<u>Period of Storage after Exposure to Antiozonant (2 loops each)</u>	<u>Days to Macroscopic Cracking of the 2 loops</u>
1. 2 hours	1, 1
2. 5 days	1, 32
3. 15 days	23, 39

b) Effect of Stress on Protection Gained through Exposure of SBR-1500 to Antiozonant Vapors.

Method: Two loops already formed and two flat strips were enclosed in a pint jar with five grams DETA for 3 days at room temperature. Then the flat strips were formed into loops and all four loops exposed to 100 pphm ozone.

<u>Specimen Identification</u>	<u>Days to Macroscopic Cracking</u>
Pre-formed loops	3 103
Loops formed after exposure to antiozonant	1 1

c) Ozone Cracking of SBR-1500 Conditioned by Pre-exposure to Very Low Concentrations of O_3 at 40°C.

Method: SBR loops both with and without wax were placed for a week in the ozone box enclosed in jars vented with one 5.5 mm. hole. Then they were directly exposed to 100 pphm ozone together with control loops which had received either no special conditioning or conditioning of seven days at 40°C.

D-55

Cracking after 16 Hrs. exposure
to 100 pphm ozone

<u>Identification of Specimens</u>		<u>Macroscopic Observations</u>	<u>Av. Crack depth in microns of median sections</u>
<u>I) SBR with Wax</u>			
	<u>Conditioning</u>		
1.	Mild O ₃ , 40°C. 7 days	2 deep cracks only, edge	24*
2.	"	1 crack only, edge	0*
3.	"	Cracking only on edges	20*
4.	No C ₃ , 40°C. 7 days	Severe general cracking	430
5.	None	Severe general cracking	475
6.	None	" " "	595
7.	None	" " "	460
8.	None	" " "	500

II. SBR without
Wax

1.	Mild O ₃ , 40°C, 7 days	Severe general cracking	335
2.	Mild O ₃ , 40°C, 7 days	" " "	665
3.	None	" " "	522
4.	None	" " "	695

* Crack depths are given only for microscopic cracks in median section which had developed during exposure to low O₃. No apparent cracking occurred in 16 hrs. at 100 pphm ozone. Macroscopic cracks on the edges were not included in the sectioning.

Appendix E

Photograph 1

Photograph No. 1 demonstrates the polyethylene bag test for antiozonants of several degrees of volatility. At the left is shown a test for pilled Eastozone 30 wherein the bag remains clear and the mounted samples were readily visible throughout the years test. The middle bag is a test of the more volatile N,N'-di-sec-butyl-p-pd showing only a dark coating at the bottom of the bag. The bag at the right demonstrates the complete coating of the inside of the bag by p-pd, a relatively highly volatile antiozonant.

It can be noted that the rubber loops are shielded by the protective bend of the aluminum spring clip so that direct contact with the bag is avoided.

Photograph 2

The two samples shown are the control at the bottom and the sample protected by m-phenylenediamine in the 54 week vented bag test at the top. The control showed macroscopic cracking after 16 weeks, while the sample at the top showed no visible cracking after 54 weeks. The loop pictured is representative of the loops packaged with o-, m- and p-phenylenediamine, triethylenetetramine, tetraethylenepentamine, dicyclohexylammonium nitrite, menthane diamine, Polyamine H Special, tetrabutylthiourea and furfurylamine for about a year. (Magnification is about X 4.)

Photograph 3

This photograph demonstrates protection by vapor-coating methods. The bottom sample is a picture of the unprotected control sample after direct exposure to 100 pphm ozone for less than 48 hours. (Magnification is about X 2.)

The middle sample shown is precoated with vapors of piperidinium pentamethylene dithiocarbamate and exposed for 8 days (no cracking occurred for 6 days). The loop depicts the type of cracking resulting for vapor-coated samples wherein protection against 100 pphm ozone is evidenced for 24 hours or more prior to cracking. Others which showed 1 to 4 weeks protection followed by this type of cracking (at 100 pphm ozone) were dodecylamine, tetrabutylthiourea and TEPA.

The top sample is a DETA (diethylenetriamine) coated sample showing protection against 100 pphm ozone for over two months in tests still continuing. It is representative of the 1 to 7 months protection obtained either by dip-coating or by vapor-exposure

(e.g., by packaging with antiozonant material) with the following additives:

N-n-Butyl-p-aminophenol
N,N'-Di-sec-butyl-p-pd
N,N'-Di-2-octyl-p-pd
N,N'-Di-3-(5-methylheptyl)-p-pd
Furfurylamine
Menthane diamine
Polyamine H Special
Tetraethylenepentamine
Triethylenetetramine





